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(54) **Method for producing an epoxy resin composition for use in molding photosemiconductor**

Herstellung von Epoxyharzen für Photohalbleiter

Préparation d'une composition de résine époxy utilisable pour le moulage de photoconducteur

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(56) References cited:  
**JP-A-60 137 046** **US-A- 4 732 962**

• **DATABASE WPIL, No. 88-115956 Derwent**  
**Publications Ltd, London, GB, & JP-A-63062363**  
**(Nitto Electric Ind. K. K.)**  
• **DATABASE WPI, No. 80-80854C Derwent**  
**Publications Ltd, London, GB, & DD-A-143839**  
**(VEB Pentacon Dresden)**  
• **PATENT ABSTRACTS OF JAPAN vol. 10, no. 137**  
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**EP 0 466 950 B1**

**Description**

The present invention relates to a method for molding a photosemiconductor for a photosemiconductor device free of optical unevenness, said photosemiconductor comprising an epoxy resin composition.

Conventionally, photoreceiving elements such as solid state image forming elements have generally been enclosed in ceramic packages in such a manner as to result in some spaces between the elements and the packages, to produce photosemiconductor devices. These ceramic packages, however, are defective in that the constituent materials therefor are relatively expensive and large-scale production thereof is inefficient. Therefore, resin molding which employs plastic packages are being studied. Of such resin molding techniques, molding with epoxy resin compositions in particular are extensively studied. Such epoxy resin compositions are obtained by melt-mixing epoxy resins, hardeners, curing accelerators and other additives with heating.

The Abstract of JP-A-60-137046 discloses an epoxy resin composition obtained by mixing an acid anhydride curing agent, a liquid epoxy resin and a metal salt of carboxylic acid/imidazole curing catalyst.

US-A-4732962 discloses a composition comprising a bisphenol-A type epoxy resin, an anhydride curing agent, an imidazole catalyst and optionally a filler system.

DE-A-3012523 discloses the use of epoxy/anhydride compositions for encapsulating radiation sensitive semiconductor devices.

GB-A-1350156 discloses a process for producing modified internally plasticized epoxy resins.

However, the epoxy resin compositions obtained by melt-mixing for use in the molding of photosemiconductors are defective in that the dispersion of each of the epoxy resin, hardener, and curing accelerator is insufficient so that these components have not been mixed uniformly to the molecular level. For this reason, if transfer molding, for example, is carried out using such an epoxy resin composition for photosemiconductor molding, the following problem is caused. As Fig. 3 illustrates, an epoxy resin composition in tablet form for photosemiconductor molding is fed to a cull 1 and pressed by a plunger 2, upon which the epoxy resin composition flows, as the arrows show, through a runner 3 into a cavity 4. As Fig. 4 illustrates, the epoxy resin composition for photosemiconductor molding passes through a gate 5 and flows into the cavity 4, where a solid state image forming element 7 mounted on a frame 6 in the cavity 4 is molded with the epoxy resin composition, as the arrows show.

In practicing this resin molding, when the epoxy resin composition for photosemiconductor molding is cured in the cavity 4, the curing reaction proceeds at higher rates in some parts and at lower rates in other parts because the dispersion of each component in the epoxy resin composition is not uniform when viewed on a molecular level. Such uneven rates of the curing reaction result in unevenness in the density of the cured molding resin, and this causes a problem that the refractive index of the molding resin varies in a wide range and the molding resin has optical unevenness which appears as a striped pattern extending in the direction of the resin flow. If, for example, an area sensor of the solid state image forming element 7 is molded with a conventional epoxy resin composition for photosemiconductor molding by the method described above and intense parallel light rays are allowed to strike upon the molded area sensor with an iris diaphragm of F-32, such optical unevenness in the molding resin as that described above causes the resulting image to have a striped pattern.

Under these circumstances, the present inventors conducted a series of extensive studies in order to eliminate optical unevenness from the cured resins obtained from epoxy resin compositions for use in photosemiconductor molding. As a result, it was found that the formation of optical unevenness is greatly affected by the refractive index distribution of the cured resin. Further studies have been made with regard to refractive index distribution and, as a result, it has now been found that a cured resin with no optical unevenness can be obtained by making the refractive index distribution curve of the cured resin sharp so as to satisfy the specific requirements (A), (B), and (C) described later. The present invention has been completed based on the above finding.

Accordingly, an object of the present invention is to provide a method for molding photosemiconductors for a photosemiconductor device free from optical unevenness.

The present invention relates to a method for molding photosemiconductors comprising producing an epoxy resin composition comprising the steps of:

(a) dissolving into an organic solvent a B-stage epoxy resin, a hardener, and a curing accelerator as constituent ingredients, and then removing the organic solvent to such a degree that the amount of the solvent remaining unremoved becomes 3% by weight or less based on the total amount of the epoxy resin composition, or

(b) dissolving an epoxy resin, a hardener, and a curing accelerator into an organic solvent, and then heating the solution to allow the curing reaction of the epoxy resin to proceed to produce a B-stage epoxy resin composition and then removing the organic solvent to such a degree that the amount of the solvent remaining unremoved becomes 3% by weight or less based on the total amount of the epoxy resin composition, or

(c) mixing one kind of epoxy resin and one kind of hardener with an organic solvent, removing the organic solvent to such a degree that the amount of the solvent remaining unremoved becomes 3% by weight or less, based on the total amount of the epoxy resin composition, and then allowing the residual epoxy resin composition to undergo the curing reaction of the epoxy resin to produce a B-stage epoxy resin composition.

The epoxy resin composition obtained by the process for molding photosemiconductors according to the present invention can be used for a photosemiconductor device comprising said photosemiconductor element molded with said cured transparent epoxy resin composition. The cured transparent epoxy resin composition obtained by the method according to the present invention has a refractive index distribution curve characterised by the following (A), (B), and (C):

(A) the refractive index difference X between refractive index values (b) and (c), which respectively are lower and higher than refractive index value (a) corresponding to the maximum peak of the refractive index distribution curve and respectively correspond to those points on the refractive index distribution curve which have a relative height of 20 with the height of the maximum peak being taken as 100, is 0.0018 or less;

(B) the refractive index difference Y, which is the larger one of the difference between the refractive index values (a) and (b) and the difference between the refractive index values (a) and (c), is 0.0012 or less; and

(C) in the case where the refractive index distribution curve has other peak or peaks than the maximum peak corresponding to the refractive index value (a), the refractive index difference Z, which is the largest one of the differences between the refractive index value (a) and refractive index values (d, ..., d<sub>n</sub>) corresponding to the other peak or peaks, is 0.0010 or less.

In the following the drawings are briefly described.

Fig. 1 is a refractive index distribution curve having the maximum peak only;

Fig. 2 is a refractive index distribution curve having the maximum peak and other peak;

Fig. 3 is a schematic view illustrating the flow of a conventional, photosemiconductor-molding epoxy resin composition being used in transfer molding;

Fig. 4 is a schematic view illustrating the resin composition flow in the pivotal part of the transfer molding machine shown in Fig. 3;

Fig. 5 is a vertical sectional view of a photosemiconductor device molded in an epoxy resin composition of this invention for photosemiconductor molding;

Fig. 6 is a diagrammatic view illustrating the principle in a refractive index-measuring apparatus; and

Figs. 7, 8, 9, 10, 11, 12, and 13 show refractive index distribution curves.

The present invention is described below in detail.

In the photosemiconductor device according to the invention, a photosemiconductor element is molded in a cured transparent epoxy resin composition which satisfies the above requirements (A), (B) and (C).

The cured resin satisfying the requirements (A), (B), and (C) has a narrower refractive index distribution, i.e., a sharper refractive index distribution curve, than the cured resins obtained from conventional epoxy resin compositions.

The requirements (A), (B), and (C) are explained below with reference to Figures. In Fig. 1, which is a bell-shaped refractive index distribution curve of one example of the cured transparent epoxy resin composition employed in the present invention, K indicates the refractive index distribution curve, (a) indicates the refractive index value corresponding to the maximum peak of the distribution curve, (b) and (c) indicate refractive index values respectively corresponding to those points on the refractive index distribution curve which have a relative height of 20 with the height of the maximum peak being taken as 100 and which respectively are on the left and right of the maximum peak, X is the refractive index difference between the refractive index values (b) and (c), and Y is the refractive index difference which is the larger one of the difference between the refractive index value (a) corresponding to the maximum peak and the refractive index value (b) and the difference between the refractive index values (a) and (c) (in the figure, Y is the difference between (a) and (c) because this difference is larger than the difference between (a) and (b)).

Even if the refractive index distribution curve has a peak (a') other than the maximum peak (a), as shown in Fig. 2, no optical unevenness results as long as the refractive index distribution curve satisfies the above requirements (A) and (B). However, in the case where the picture element numbers for the present-day solid state image forming elements are increased greatly or such a function that a refractive index difference is emphasized by means of a microlens is imparted to photosemiconductor devices, the presence of a peak (a') other than the maximum peak (a) may cause a problem. Even in such a case where a refractive index distribution curve has two or more peaks, the cured resin can be made applicable to future solid state image forming elements which may possibly have greatly increased picture element numbers, without causing problems ascribable to optical unevenness, by regulating the refractive index dif-

ference Z, which is the largest one of the differences between the refractive index value (a) corresponding to the maximum peak and refractive index value(s) corresponding to the other peak(s) (in Fig. 2, Z is the refractive index difference between (a) and (a')), at 0.0010 or less, preferably at 0.0003 or less.

The refractive index curves shown in Figs. 1 and 2 referred to above can be obtained by measurement with a refractive index-measuring apparatus utilizing the principle shown in Fig. 6. In Fig. 6, F indicates an interference filter, SL a spectral illuminant lamp, S<sub>1</sub> an inlet slit, S<sub>2</sub> an outlet slit, L<sub>1</sub> a collimator lens, L<sub>2</sub> a telemeter lens, P a V-block prism, SM a sample to be tested, P.M a photomultiplier, and N a telemeter part.

For measurement with this refractometer, a cured transparent epoxy resin composition is formed, for example, into a cubic sample SM, two adjacent sides of the cubic sample are polished by buffing so as to have a surface roughness of 1.5  $\mu\text{m}$  or less, and this sample is set on the V-block prism P having a V-shaped depression with the polished sides of the sample being in contact with the V-shaped depression walls. Then, light is emitted from the illuminant SL. The light emitted from the illuminant SL is converted to monochromatic light by the interference filter F, and the monochromatic light passes through the inlet slit S<sub>1</sub> and then converted to parallel rays of light by the collimator lens L<sub>1</sub>. The parallel light rays pass through the V-block prism P, the sample SM, and the V-block prism P in this order, while the parallel light rays are being polarized upward and downward relative to the light axis due to the difference in refractive index between the V-block prism P and the sample SM. The telemeter part N, equipped with the telemeter lens L<sub>2</sub>, the outlet slit S<sub>2</sub>, and the photomultiplier P.M, oscillates as shown by the arrows by means of a pulse motor (not shown) and receives the polarized light at each position in the oscillation movement, and the amount of the received light is indicated on a display (not shown) as the amount of energy. For this measurement, the relationship between refractive index and each angle in the above oscillation movement has been determined beforehand. Therefore, the amount of light received at a given angle means the amount of light refracted at an angle corresponding to that given angle.

Examples of this refractive index-measuring apparatus includes that produced and marketed by Karunew Optics Company, Japan under the trade name of Automatic Refractometer KPR-200. The measurement of refractive index in the present invention is made by means of this refractometer with sodium D-line (589.6 nm) being used as the measuring light.

The cured transparent epoxy resin composition free of optical unevenness is one whose refractive index distribution curve obtained by the method as described above is sharp and satisfies the requirements (A), (B), and (C) described hereinabove.

An epoxy resin composition which can cure into a resin having such a sharp refractive index distribution curve may be produced, for example, by uniformly dispersing each of the constituent ingredients in the epoxy resin composition.

Examples of the technique of uniformly dispersing ingredients to produce an epoxy resin composition for use in photosemiconductor molding include: (1) a method in which a conventional powdery epoxy resin composition for molding use which has been made to be in the B-stage (semi-cured state) is mixed sufficiently with an organic solvent to dissolve each component, and then the organic solvent is evaporated; (2) a method in which raw ingredients such as an epoxy resin, a hardener, a curing accelerator, and others are mixed with and uniformly dissolved in an organic solvent, the resulting solution is heated so as to result in a B-stage composition, and then the solvent is evaporated; and (3) a method in which the same solution as that obtained in (2) above is prepared, subsequently the solvent is evaporated, and then the residue is heated mildly to form a B-stage composition.

In the above methods, since an epoxy resin composition or raw materials therefor are once dissolved in an organic solvent, it is possible, by the filtration of these solutions, to easily remove fine foreign substances such as dust particles, the removed of which has so far been impossible.

Furthermore, even if the refractive index distribution curve of a cured resin to be obtained from the resulting epoxy resin composition has a peak (a') other than the maximum peak (a), the other peak can be weakened by reducing the epoxy resin composition to a uniformly mixed fine powder, thereby giving a bell-shaped distribution curve having the maximum peak a only as shown in Fig. 1. The term fine powder herein normally means a powder in which particles having maximum particle diameters of 30  $\mu\text{m}$  or less, preferably 10  $\mu\text{m}$  or less, comprise 90 wt% or more of the powder.

In the above method (1), a B-stage (semi-cured) epoxy resin composition is prepared by mixing the above-mentioned ingredient. As the method for mixing the ingredients, a partial reaction method (semi-curing method) and melt-mixing method are generally used. The degree of reaction of the B-stage epoxy resin composition is generally such an extent that the gelation time of the resin composition at 150°C be from 10 to 70 seconds, and preferably from 10 to 40 seconds. Next, the B-stage epoxy resin composition is uniformly dissolved in an organic solvent. By this procedure, the ingredients of the resin composition are mixed with each other uniformly to the molecular level. The organic solvent is then removed by evaporation from the solution, and the residue is cooled to room temperature and pulverized by a conventional method. The pulverized resin composition is stamped into tablets if desired.

The degree of reaction of the thus-obtained final epoxy resin composition is generally such an extent that a transfer molding process can be carried out and that the gelation time at 150°C is from 10 to 50 seconds, and preferably from 10 to 40 seconds. In the above method, the resin composition may be heated after removing the organic solvent, for

example in order to adjust the viscosity of the resin composition. At this time, if the resin composition is heated vigorously, unevenness of the curing degree due to unevenness of the reaction rate develops. Therefore, the heating of the resin composition is preferably carried out gradually at a low temperature so that the gelation time at 150°C does not lower than 20 seconds.

5 In the above method (2), the ingredients are firstly dissolved in an organic solvent. By this procedure, the ingredients of the resin composition are mixed with each other uniformly to the molecular level. The resulting solution is heated to proceed the curing reaction so as to convert the resin composition to the B-stage. The organic solvent is then removed by evaporation from the solution, and the residue is cooled to room temperature and pulverized by a conventional method. The pulverized resin composition is stamped into tablets if desired.

10 In this method, the ingredients may be heated simultaneously with dissolving in the organic solvent but not heated after completion of dissolving. Alternatively, the B-stage resin composition may further heated to heighten the curing degree. In this method, while the resin composition may be heated after removing the organic solvent to adjust the viscosity or the like, the heating is preferably carried out gradually at a low temperature so that the gelation time at 150°C does not lower than 20 seconds because of the above reasons.

15 The degree of reaction of the thus-obtained final product is generally such an extent that the gelation time at 150°C is from 10 to 70 seconds, and preferably from 10 to 40 seconds. At this time, the extent of gelation after starting evaporation of the organic solvent is preferably controlled such that the gelation time at 150°C does not lower than 20 seconds.

20 In the above method (1) and (2), one, or two or more kinds of each ingredients may be used. The term "one kind" used herein includes, in the case of epoxy resins for example, bisphenol A type and bisphenol F type which have the same skeleton and are classified into the bisphenol type, and in the case of hardener, phthalic anhydride and tetrahydrophthalic anhydride which have the same skeleton and are classified into the phthalic acid type.

25 In the above method (3), one kind of the epoxy resin and one kind of hardener are dissolved in an organic solvent. The organic solvent is removed by evaporation from the resulting solution, and the residue is subjected to low temperature heating (low temperature aging) so as to convert the residue into B-stage. In this method, because one kind of the epoxy resin and one kind of hardener are use, only one kind the cured product is produced. Thus, unevenness of curing degree is not formed and optical unevenness is not formed.

30 In this method, if the low temperature aging is carried out gradually at a low temperature so that the gelation time at 150°C does not lower than 20 seconds, optical unevenness is substantially not formed even though two or more kinds of each ingredients are used.

The degree of reaction of the thus-obtained final product is generally such an extent that the gelation time at 150°C is from 10 to 70 seconds, and preferably from 10 to 40 seconds. At this time, the extent of gelation after starting evaporation of the organic solvent is preferably controlled such that the gelation time at 150°C does not lower than 20 seconds.

35 The epoxy resin composition for photosemiconductor molding to be used for producing the photosemiconductor device according to the present invention is one which is obtained by use of an epoxy resin, a hardener, and a curing accelerator, and contains no inorganic fillers such as silica powder.

40 As the epoxy resin, conventionally known epoxy resins may be used without any particular limitation as long as the epoxy used and the resulting cured composition are less apt to undergo discoloration. Examples of such epoxy resins include bisphenol A epoxy resins, bisphenol F epoxy resins, phenol-novolac epoxy resins, alicyclic epoxy resins, heterocycle-containing epoxy resins such as triglycidyl isocyanurate and hydantoin epoxies, hydrogenated bisphenol A epoxy resins, aliphatic epoxy resins, glycidyl ether epoxy resins, and the like. These may be used alone or in combination.

45 As the hardener, known hardeners for epoxy resins can be used without any particular limitation. However, acid anhydrides are advantageous in that they are less apt to cause discoloration of the resin composition during or after cure. Examples of such acid anhydrides include phthalic anhydride, maleic anhydride, trimellitic anhydride, pyromellitic anhydride, hexahydrophthalic anhydride, tetrahydrophthalic anhydride, methylnadic anhydride, nadic anhydride and glutaric anhydride. Other examples of the hardener include amine-type hardeners such as m-phenylenediamine, dimethyldiphenylmethane, diaminodiphenyl sulfone, m-xylenediamine, tetraethylenepentamine, diethylamine and propylamine, and further include phenolic resin-type hardeners. Any of these may be employed.

50 In the present invention, the combination in which the epoxy resin is at least one of bisphenol A epoxy resin and bisphenol F epoxy resin, and the hardener is at least one of phthalic anhydride and tetrahydrophthalic anhydride is preferred.

55 Examples of the curing accelerator include tertiary amines, imidazole and its derivatives, metal salts of carboxylic acids and phosphorus compounds.

Besides the above-described ingredients, conventionally known additives such as anti-discoloring agents, modifiers, anti-deteriorating agents and mold-release agents, may be incorporated, if required and necessary, into the epoxy resin composition for photosemiconductor molding according to this invention.

As the anti-discoloring agent, conventionally known ones may be mentioned, such as phenolic compounds, amine-type compounds, organosulfur compounds and phosphine-type compounds.

The organic solvent to be used for producing the epoxy resin composition is not particularly limited as long as it is capable of completely dissolving B-stage epoxy resin compositions for photosemiconductor molding. Examples of the organic solvent include hydrocarbons such as toluene and xylene, halogenated hydrocarbons such as dichloromethane, 1,1,1-trichloroethane and 1,1,2-trichloroethane, ethers such as diethyl ether, dioxane and tetrahydrofuran, ketones such as acetone, methyl ethyl ketone and diethyl ketone and mixed solvents composed of two or more thereof.

Neither the mixing ratio of the organic solvent to the epoxy resin composition for photosemiconductor molding nor the temperature for mixing is particularly limited, as long as the epoxy resin composition for photosemiconductor molding can be completely dissolved.

Generally however, the amount of the organic solvent used is preferably from 1 to 50 times by weight, more preferably from 1 to 10 times by weight, the amount of the B-stage epoxy resin composition for photosemiconductor molding. The mixing temperature is preferably kept at 100°C or lower because too high a temperature results in gelation of the epoxy resin composition for photosemiconductor molding.

Methods for removing the organic solvent in the above processes are not particularly limited. For example, there may be employed a method in which the solvent is removed under reduced pressure at ordinary temperature or with heating according to need, or a method in which the solvent is removed by freeze drying under vacuum. According to the method of the present invention, the amount of the organic solvent remaining unremoved is 3% by weight or less based on the total amount of the epoxy resin composition for photosemiconductor molding. The content of the remaining organic solvent in the epoxy resin composition is preferably 1.5% by weight or less, and particularly preferably 0.05% by weight or less. The reasons for the above are that if the content of the remaining organic solvent exceeds 3% by weight, the epoxy resin composition for photosemiconductor molding tends to have a very short pot life and the cured composition tends to have a lowered glass transition temperature and hence an increased linear expansion coefficient, so that the molding resin may have impaired moisture and heat cycle resistance.

The epoxy resin composition for photosemiconductor molding obtained by the method described above is in such a state that all the components have been mixed with each other uniformly to the molecular level. Therefore, the refractive index distribution curve of the cured composition is sharp, so that the cured composition has no optical unevenness. Furthermore, since all the components are dissolved in an organic solvent during the production process and, hence, can be easily purified e.g. by suction filtration under reduced pressure or by filtration under pressure using for example an ordinary filter paper, gel-like aggregates and foreign substances including fine dust particles present in the resin composition can be easily removed which have so far been difficult to remove.

It is preferable that the epoxy resin composition for photosemiconductor molding should be optically transparent since it is to be used in the resin molding of photosemiconductors such as photoreceiving elements. The term "transparent" used herein means that the cured resin obtained from the epoxy resin composition for photosemiconductor molding has a transmittance of generally 90% or higher, preferably 95% or higher, more preferably 98% or higher, as measured at 600 nm with the cured resin thickness being 1 mm.

The meaning of "ingredients being mixed with each other uniformly to the molecular level" is as follows. The resin composition is transfer molded at 150°C for 6 minutes and then hardened at 150°C for 3 hours. The hardened resin composition is taken out from the runner portion of the molding die, and formed into a flat plate (thickness: 3.0 mm, width: 5 mm) having a branch perpendicular to the flat plate, the surface of which is polished to have a surface roughness of 1.5  $\mu$ m or less. The plate of the cured resin composition is equipped on a solid state image forming element (1/2 inch, 380,000 picture elements). Intense parallel light rays having a luminous intensity of 10 candelas are allowed to strike the image forming element with an iris diaphragm of F-32. The case where no striped pattern is observed is determined as "mixed uniformly to the molecular level".

Molding of photoreceiving elements or other photosemiconductors with the epoxy resin composition is not particularly limited, and can be carried out by known molding techniques such as, for example, ordinary transfer molding. In practicing the transfer molding, a molding resin composition in a powder form is normally used after being tableted at ordinary temperature.

In the transfer molded resin composition of the present invention, because the ingredients are mixed with each other uniformly to the molecular level, curing unevenness and optical unevenness are not formed although such unevenness is formed in conventional resin composition.

The photosemiconductor device thus obtained, for example, has a structure as shown in Fig. 5, in which an image-pickup solid element 13 as a photoreceiving element is mounted on a bonding pad 11 through an adhesive 12, and a color filter 15 is bonded to the upper side of the photoreceiving element by means of a transparent adhesive 14, with this assembly being resin-molded in an epoxy resin composition 16 for photosemiconductor molding. The color filter 15 has been provided in order to obtain color images, and is unnecessary for monochromatic images. In the figure, numeral 17 denotes a glass plate, 18 a bonding wire, and 19 a lead frame.

Since this photosemiconductor device has been resin-molded in a photosemiconductor-molding epoxy resin com-

position in which all the components thereof have been mixed uniformly to the molecular level, the refractive index distribution curve of the molding resin 16 is sharp, so that the molding resin 16 has no optical unevenness. Therefore, images obtained by operating this device are free from striped patterns ascribable to optical unevenness and black spots due to inclusion of foreign particles. The freedom of optical unevenness has been ascertained with photoconductor devices obtained by regulating the thickness  $\ell$  of the molding resin over the color filter 15 at ordinary values, i.e., 0.5 to 2 mm.

As described above, the photosemiconductor device of the present invention is free of optical unevenness because the refractive index distribution curve of the cured transparent epoxy resin composition is characterized by (A), (B), and (C) described hereinabove. Furthermore, in the case where the cured transparent epoxy resin is obtained from an epoxy resin composition which has undergone a dissolved state in an organic solvent, foreign substances can be removed from the resin composition by filtration, so that the cured resin can be made free of gel-like aggregates and foreign substances, such as fine dust particles, present in the resin composition, although these impurities have so far been difficult to remove. Thus, the resin composition can be of high quality. Therefore, such a high-quality epoxy resin composition is used for resin-molding of a photoreceiving element, such as a solid state image forming element, to produce a photosemiconductor device according to the present invention, the images formed by the photosemiconductor device are free from striped patterns ascribable to optical unevenness of molding resin or black spots ascribable to foreign substances present in molding resin. That is, the photosemiconductor device of the present invention, although being of a resin-molded type, has high performance that is equal to or higher than those of ceramic-packaged types.

The present invention will be explained below in more detail by reference to the following Examples and Comparative Examples, but the Examples should not be construed to be limiting the scope of the invention. Hereinafter, all parts are by weight.

#### EXAMPLES 1 TO 4 AND COMPARATIVE EXAMPLES 1 TO 3

For use in the Examples and Comparative Examples, epoxy resin compositions A to G were prepared beforehand by the methods given below in which the six formulations shown in Table 1 were used. In Table 1, the formulations are indicated in terms of part by weight.

Table 1

Formulation	Epoxy resin		Hardener	Catalyst <sup>4</sup>
	Epikote 1001 <sup>1</sup>	Triglycidyl isocyanurate <sup>2</sup>	tetrahydrophthalic anhydride <sup>3</sup>	
1	75	25	52.0	0.3
2	75	25	51.9	0.3
3	75	25	51.8	0.3
4	75	25	51.7	0.3
5	75	25	51.4	0.3
6	75	25	51.0	0.3

Note:

<sup>1</sup>1 Manufactured by Yuka Shell Epoxy K.K., Japan

<sup>2</sup>2 Manufactured by Nissan Chemical Industries, Ltd., Japan

<sup>3</sup>3 Manufactured by Hitachi Chemical Co., Ltd., Japan

<sup>4</sup>4 "2E4MZ" manufactured by Shikoku Chemical Co., Ltd., Japan

#### Epoxy Resin Composition A

The ingredients shown under formulation 1 in Table 1 were melt-mixed with heating in the respective proportions shown in the table, and then the mixture was allowed to undergo curing reactions of the epoxy resins, thereby preparing a B-stage epoxy resin composition for photosemiconductor molding which composition had a gelation time as measured at 150°C of 30 seconds. This B-stage epoxy resin composition for photosemiconductor molding was completely dissolved in the organic solvent whose kind and amount are shown in Table 2 given later, and then the solvent was removed under reduced pressure, while the solution was being heated at 45°C. The resulting residue was reduced to powder to obtain photosemiconductor-molding epoxy resin composition A in a powder form (for Example 1) having the residual organic solvent content as shown in Table 2 and a gelation time as measured at 150°C of 25 seconds.

Epoxy Resin Composition B

Two compositions were prepared according to formulations 1 and 3, respectively, as shown in Table 1. Each of the two compositions was allowed to undergo curing reactions of the epoxy resins thereby to prepare, from each composition, a B-stage epoxy resin composition for photosemiconductor molding which composition had a gelation time as measured at 150°C of 30 seconds. 50 Parts each of the thus-prepared two kinds of B-stage epoxy resin compositions for photosemiconductor molding were blended with each other, and the blend was mixed with and completely dissolved in the organic solvent whose kind and amount are shown in Table 2. The solvent was then removed under reduced pressure, while the solution was being heated at 45°C. The resulting residue was reduced to powder to obtain photosemiconductor-molding epoxy resin composition B in a powder form (for Example 2) having the residual organic solvent content as shown in Table 2 and a gelation time as measured at 150°C of 25 seconds.

Epoxy Resin Composition C

The ingredients shown under formulation 2 in Table 1 were melt-mixed with heating, and then the mixture was allowed to undergo curing reactions of the epoxy resins, thereby preparing a B-stage epoxy resin composition for photosemiconductor molding which composition had a gelation time as measured at 150°C of 30 seconds. This B-stage epoxy resin composition for semiconductor molding was mixed with and completely dissolved in the organic solvent whose kind and amount are shown in Table 2. The solvent was then removed under reduced pressure, while the solution was being heated at 45°C. The resulting residue was reduced to powder to obtain photosemiconductor-molding epoxy resin composition in a powder form having the residual organic solvent content as shown in Table 2 and a gelation time as measured at 150°C of 25 seconds. 40 Parts of this epoxy resin composition was dryblended with 60 parts of the above-described epoxy resin composition A to obtain photosemiconductor-molding epoxy resin composition C (for Example 3).

Epoxy Resin Composition D

The ingredients shown under formulation 4 in Table 1 were melt-mixed with heating, and then the mixture was allowed to undergo curing reactions of the epoxy resins, thereby preparing a B-stage epoxy resin composition for photosemiconductor molding which composition had a gelation time as measured at 150°C of 30 seconds. This B-stage epoxy resin composition for photosemiconductor molding was mixed with and completely dissolved in the organic solvent whose kind and amount are shown in Table 2. The solvent was then removed under reduced pressure, while the solution was being heated at 45°C. The resulting residue was reduced to powder to obtain photosemiconductor-molding epoxy resin composition in a powder form having the residual organic solvent content as shown in Table 2 and a gelation time as measured at 150°C of 25 seconds. 40 Parts of this epoxy resin composition was dryblended with 60 parts of the above-described epoxy resin composition A to obtain photosemiconductor-molding epoxy resin composition D (for Example 4).

Epoxy Resin Composition E

The ingredients shown under formulation 5 in Table 1 were melt-mixed with heating without using an organic solvent, and then the mixture was allowed to undergo curing reactions of the epoxy resins. The resulting mixture was reduced to powder to obtain photosemiconductor-molding epoxy resin composition E in a powder form (for Comparative Example 1) having a gelation time as measured at 150°C of 25 seconds.

Epoxy Resin Composition F

The ingredients shown under formulation 5 in Table 1 were melt-mixed with heating, and then the mixture was allowed to undergo curing reactions of the epoxy resins, thereby preparing a B-stage epoxy resin composition for photosemiconductor molding which composition had a gelation time as measured at 150°C of 30 seconds. This composition was reduced to powder. 35 Parts of the thus-obtained powdery epoxy resin composition was dryblended with 65 parts of the above-described composition A to obtain epoxy resin composition F (for Comparative Example 2).

Epoxy Resin Composition G

The ingredients shown under formulation 6 in Table 1 were melt-mixed with heating, and then the mixture was allowed to undergo curing reactions of the epoxy resins, thereby preparing a B-stage epoxy resin composition for photosemiconductor molding which composition had a gelation time as measured at 150°C of 30 seconds. This com-



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position was reduced to powder. 20 Parts of the thus-obtained powdery epoxy resin composition was dryblended with 80 parts of the above-described epoxy resin composition A to obtain epoxy resin composition G (for Comparative Example 3).

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Table 2

	Example			Comparative Example		
	1	2	3	1	2	3
Epoxy resin composition (part by weight)	A	B	C	D	E	F
Organic solvent (dichloromethane) (part by weight)	500	500	500	500	-	-
Residual organic solvent content (wt%)	1	1	1	1	-	0.80
Refractive index difference X	0.0015	0.0018	0.0015	0.0015	0.0021	0.0018
Refractive index difference Y	0.0010	0.0010	0.0010	0.0010	0.0010	0.0012
Refractive index difference Z	-	-	0.0002	0.0006	-	0.0008
Optical unevenness A	none	none	none	none	present	present
Optical unevenness B	none	slightly present	none	slightly present	present	present

## (Refractive Index Measurement)

Each of the seven kinds of powdery epoxy resin compositions (A to G) obtained by the methods described above was formed into tablets. Each tableted composition was subjected to transfer molding at 150°C for 6 minutes to form a cube, which was then cured at 150°C for 3 hours. Thus, seven cured cubes each measuring 1 x 1 x 1 cm were prepared from the seven kinds of compositions. With respect to each of these cured cubes, adjacent two sides were polished by buffing so that the polished surfaces had surface roughnesses of 1.5  $\mu\text{m}$  or less. The thus-obtained cubic samples (A to G) were examined for refractive index distribution by means of a refractometer (Automatic Refractometer KPR-200 manufactured by Karunew Optics Company).

The results of the refractive index measurement on these samples A to G are shown in Figs. 7 to 13, respectively; samples A to D are for Examples, while samples E to G are for Comparative Examples.

It is apparent, from the refractive index distribution curves for samples A to D as shown in Figs. 7 to 10 and from the values of X, Y, and Z in Table 2, that samples A to D satisfy requirements (A), (B), and (C) which are essential in the present invention. In particular, in the case of samples C and D, the refractive index distribution curves as shown in Figs. 9 and 10 have peaks other than the maximum peaks, but the refractive index differences Z between the refractive index value (a) corresponding to the maximum peak and the refractive index value (a') corresponding to the other peak are within the specific range, i.e., 0.0010 or less, as apparent from Figs. 9 and 10 and the values of Z in Table 2. By contrast, comparative samples E and F do not satisfy requirement (A) or (B) described hereinabove as apparent from the refractive index distribution curves shown in Figs. 11 and 12 and from the values of X and Y shown in Table 2. The other comparative sample G satisfies requirements (A) and (B) as seen from the refractive index distribution curve shown in Fig. 13 and from the values of X and Y in Table 2, but the refractive index difference Z between the refractive index value (a) corresponding to the maximum peak and the refractive index value (a') corresponding to the other peak is above 0.0010. That is, sample G does not satisfy requirement (C) described hereinabove.

## (Preparation of Photosemiconductor Device)

Using each of the seven kinds of powdery epoxy resin compositions (A to G), a photosemiconductor device was prepared by actually subjecting an area sensor, which is an image-pickup solid element, to direct molding at 150°C for 6 minutes, followed by postcure at 150°C for 3 hours. Using this photosemiconductor device, a camera was constructed. Upon this camera, intense parallel rays of light (luminous intensity: 10 candelas) were allowed to strike at a right angle, and images taken at an iris of F-32 were projected on a display. As a result, the four kinds of cameras constructed in Examples respectively using compositions A to D gave images free from optical unevenness as shown in Table 2 (Optical unevenness A). By contrast, in the case of the three kinds of cameras of Comparative Examples constructed by using compositions E to G, respectively, optical unevenness was observed on the images with part of the images having a striped pattern.

Furthermore, using each of the runner-shaped plates (thickness 3.0 mm, width 5 mm) which remained in the runner part of the mold after the direct molding described above, occurrence of optical unevenness was examined as follows. That is, a runner-shaped plate which had a surface polished to a surface roughness of 1.5  $\mu\text{m}$  or less and had a part curved at 120° was placed on a molded area sensor which was an solid state image forming element of the type having 380,000 picture elements per 1/2 inch and which had been incorporated into a camera, and then intense parallel light rays were allowed to strike upon the plate at a right angle to examine the resulting images for a striped pattern at an iris of F-32.

In view of the fact that sample polymers formed in the runner part were as thick as 3.0 mm and were hence more apt to cause a striped pattern, this optical unevenness test is severer than the above-described optical unevenness evaluation and can be thought to be a test that examined as to whether the sample would be applicable to future solid state image forming elements expected to have an increased number of picture elements. As a result, the resin plates of Examples 1 and 3 obtained from the above-described epoxy resin compositions A and C, respectively, caused no striped pattern on the images taken by the cameras, i.e., the two resin plates were free from optical unevenness, while the resin plates of Examples 2 and 4 obtained from compositions B and D, respectively, caused striped patterns to a slight degree, as shown in Table 2 (Optical unevenness B). In contrast thereto, all of the resin plates of Comparative Examples respectively obtained from compositions E to G caused striped patterns.

## Claims

1. A method for molding photosemiconductors comprising producing an epoxy resin composition comprising the steps of:

(a) dissolving into an organic solvent a B-stage epoxy resin, a hardener, and a curing accelerator as constituent ingredients, and then removing the organic solvent to such a degree that the amount of the solvent remaining unremoved becomes 3% by weight or less based on the total amount of the epoxy resin composition, or

5 (b) dissolving an epoxy resin, a hardener, and a curing accelerator into an organic solvent, and then heating the solution to allow the curing reaction of the epoxy resin to proceed to produce a B-stage epoxy resin composition and then removing the organic solvent to such a degree that the amount of the solvent remaining unremoved becomes 3% by weight or less based on the total amount of the epoxy resin composition, or

10 (c) mixing one kind of epoxy resin and one kind of hardener with an organic solvent, removing the organic solvent to such a degree that the amount of the solvent remaining unremoved becomes 3% by weight or less, based on the total amount of the epoxy resin composition, and then allowing the residual epoxy resin composition to undergo the curing reaction of the epoxy resin to produce a B-stage epoxy resin composition.

15 2. The method of claim 1, wherein said epoxy resin is at least one member selected from the group consisting of bisphenol A epoxy resins and bisphenol F epoxy resins, and said hardener is at least one member selected from the group consisting of phthalic anhydride and tetrahydrophthalic anhydride.

20 3. The method of claim 1, wherein the amount of said organic solvent remaining unremoved is 1.5% by weight or less based on the total amount of the epoxy resin composition.

25 4. The method of claim 3, wherein the amount of the organic solvent remaining unremoved is 0.05% by weight or less based on the total amount of the epoxy resin composition.

5. The use of an epoxy resin composition obtained by the method of any of claims 1 to 4 for molding a photoconductor element for a photoconductor device.

## Patentansprüche

35 1. Verfahren zum Formen von Photohalbleitern, umfassend die Herstellung einer Epoxidharzmasse, umfassend die Schritte:

(a) Auflösen eines B-Stufen-Epoxidharzes, eines Härters und eines Härtungsbeschleunigers als Bestandteile in einem organischen Lösungsmittel und anschließend Entfernen des organischen Lösungsmittels in einem Ausmaß, daß die Menge des verbliebenen, nicht entfernten Lösungsmittels 3 Gewichtsprozent oder weniger wird, bezogen auf die Gesamtmenge der Epoxidharzmasse, oder

40 (b) Auflösen eines Epoxidharzes, eines Härters und eines Härtungsbeschleunigers in einem organischen Lösungsmittel und anschließend Erhitzen der Lösung, damit die Härtungsreaktion des Epoxidharzes unter Herstellung einer Epoxidharzmasse der B-Stufe voranschreitet, und danach Entfernen des organischen Lösungsmittels in einem Ausmaß, daß die Menge des verbliebenen, nicht entfernten Lösungsmittels 3 Gewichtsprozent oder weniger wird, bezogen auf die Gesamtmenge der Epoxidharzmasse, oder

45 (c) Vermischen einer Art Epoxidharz und einer Art Härter mit einem organischen Lösungsmittel, Entfernen des organischen Lösungsmittels in einem Ausmaß, daß die Menge des verbliebenen, nicht entfernten Lösungsmittels 3 Gewichtsprozent oder weniger wird, bezogen auf die Gesamtmenge der Epoxidharzmasse, und anschließend Härtenlassen des Epoxidharzes der zurückbleibenden Epoxidharzmasse unter Herstellung einer Epoxidharzmasse der B-Stufe.

50 2. Verfahren nach Anspruch 1, wobei das Epoxidharz mindestens ein Mitglied, ausgewählt aus der Gruppe, bestehend aus Bisphenol-A-Epoxidharzen und Bisphenol-F-Epoxidharzen, ist und wobei der Härter mindestens ein Mitglied, ausgewählt aus der Gruppe, bestehend aus Phthalsäureanhydrid und Tetrahydrophthalsäureanhydrid, ist.

55 3. Verfahren nach Anspruch 1, wobei die Menge des verbliebenen, nicht entfernten, organischen Lösungsmittels 1,5 Gewichtsprozent oder weniger, bezogen auf die Gesamtmenge der Epoxidharzmasse, ist.

4. Verfahren nach Anspruch 3, wobei die Menge des verbliebenen, nicht entfernten, organischen Lösungsmittels 0,05 Gewichtsprozent oder weniger, bezogen auf die Gesamtmenge der Epoxidharzmasse, ist.
5. Verwendung einer Epoxidharzmasse, erhalten durch das Verfahren nach einem der Ansprüche 1 bis 4, zum Formen eines Photohalbleiterelements für eine Photohalbleitervorrichtung.

# Revendications

1. Procédé de moulage de photoconducteurs comprenant la préparation d'une composition de résine époxy comprenant les étapes de:
  - (a) la dissolution dans un solvant organique d'une résine époxy à l'état B, d'un durcisseur et d'un accélérateur de durcissement comme ingrédients constitutifs, et ensuite l'élimination du solvant organique à un degré tel que la quantité de solvant restant non éliminé soit de 3 % en poids ou moins sur la base de la quantité totale de la composition de résine époxy, ou
  - (b) la dissolution d'une résine époxy, d'un durcisseur, et d'un accélérateur de durcissement dans un solvant organique, et ensuite le chauffage de la solution pour permettre la réaction de durcissement de la résine époxy pour procéder à la préparation d'une composition de résine époxy à l'état B et ensuite l'élimination du solvant organique à un degré tel que la quantité de solvant restant non éliminé soit de 3 % en poids ou moins sur la base de la quantité totale de la composition de résine époxy, ou
  - (c) le mélange d'une sorte de résine époxy et d'une sorte de durcisseur avec un solvant organique, l'élimination du solvant organique à un degré tel que la quantité de solvant restant non éliminé soit de 3 % en poids ou moins, sur la base de la quantité totale de la composition de résine époxy, et ensuite en laissant la composition de résine époxy résiduelle subir la réaction de durcissement de la résine époxy pour produire une composition de résine époxy à l'état B.
2. Procédé selon la revendication 1, caractérisé en ce que ladite résine époxy est au moins un membre choisi dans le groupe consistant en résines époxy bisphénol A et résines époxy bisphénol F, et ledit durcisseur est au moins un membre choisi dans le groupe consistant en anhydride phtalique et anhydride tétrahydrophthalique.
3. Procédé selon la revendication 1, caractérisé en ce que la quantité dudit solvant organique restant non éliminé est de 1,5 % en poids ou moins sur la base de la quantité totale de la composition de résine époxy.
4. Procédé selon la revendication 3, caractérisé en ce que la quantité du solvant organique restant non éliminé est de 0,05 % en poids ou moins sur la base de la quantité totale de la composition de résine époxy.
5. Utilisation d'une composition de résine époxy obtenue par le procédé selon l'une quelconque des revendications 1 à 4 pour le moulage d'un élément photoconducteur pour un dispositif photoconducteur.

Fig. 1

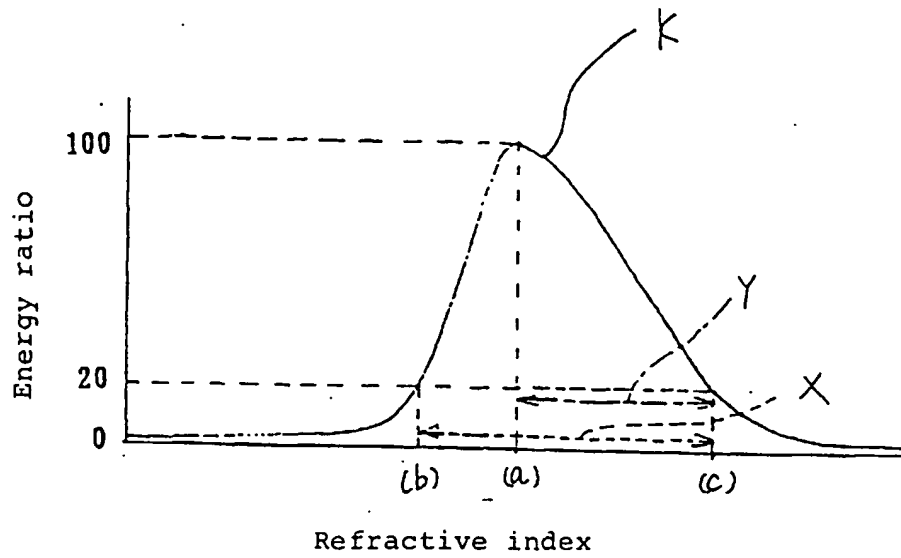


Fig. 2

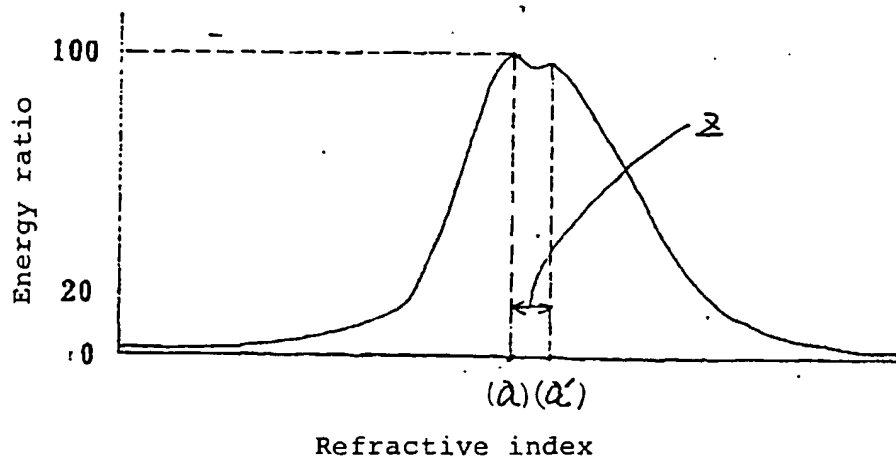


Fig. 3

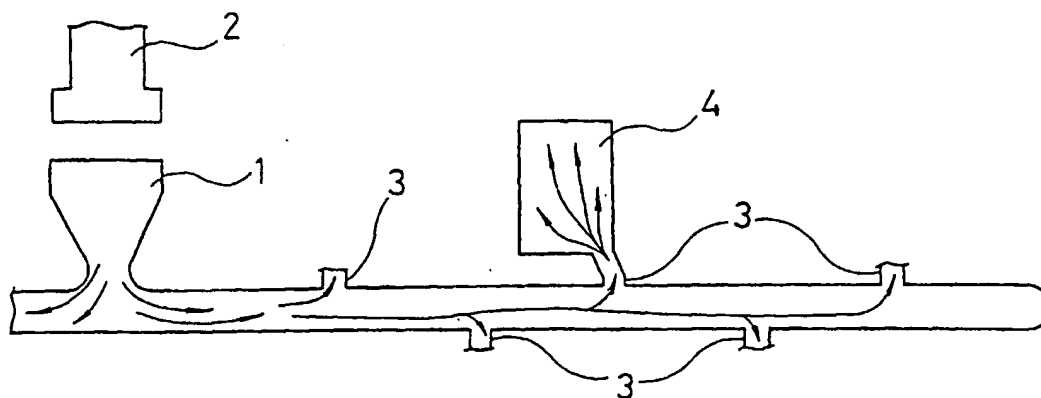


Fig. 4

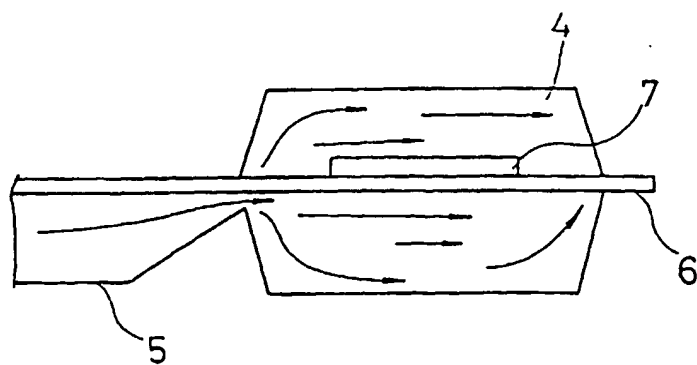


Fig. 5

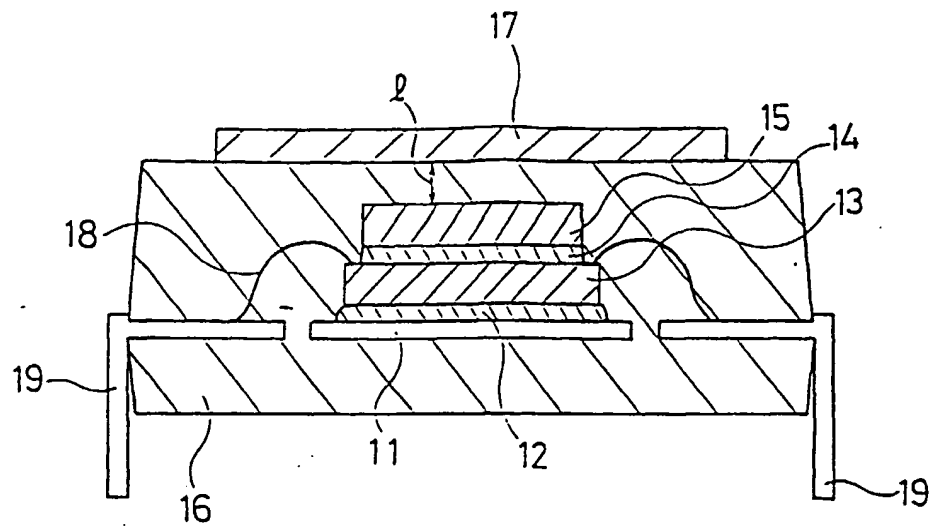




Fig. 6

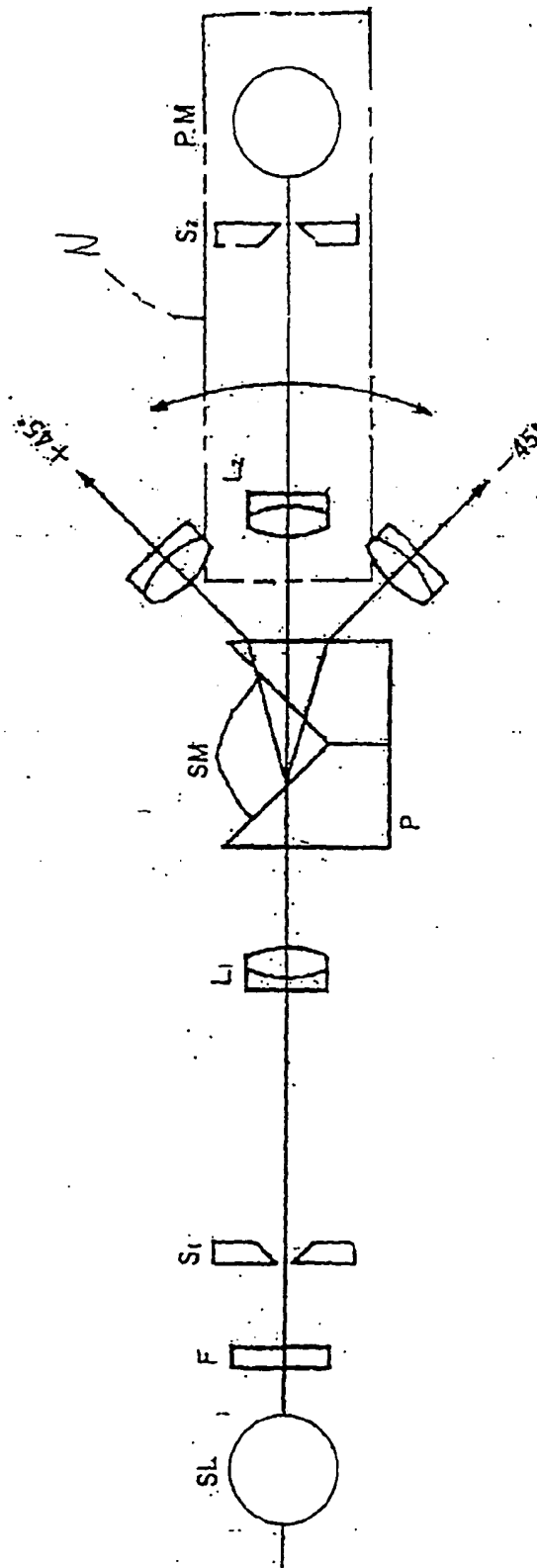


Fig. 7

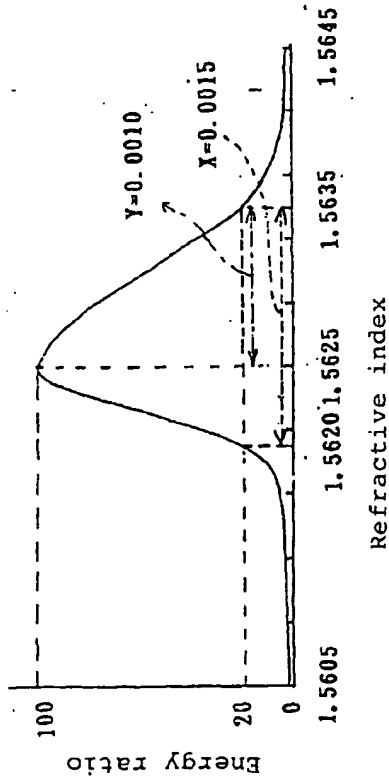


Fig. 8

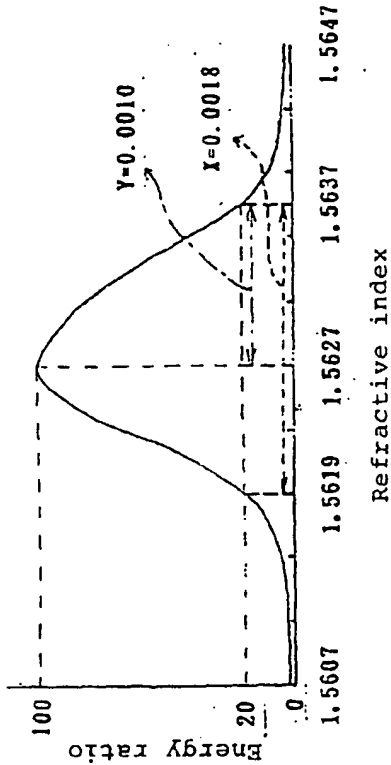


Fig. 9

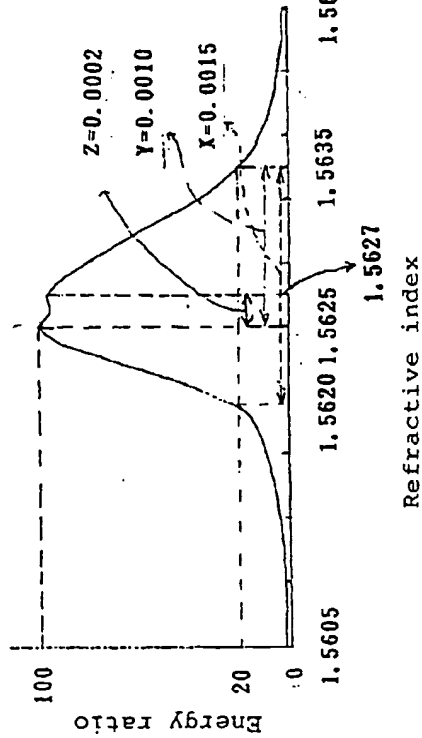


Fig. 10

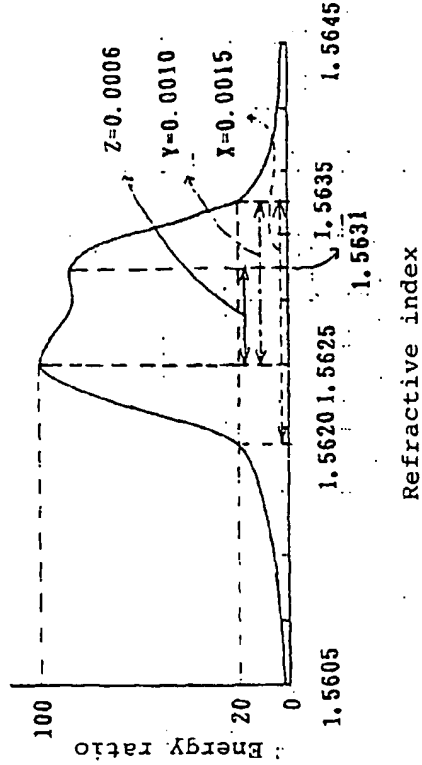


Fig. 12

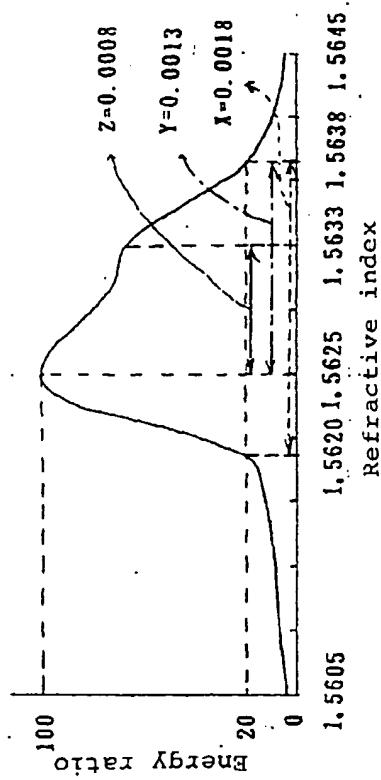


Fig. 11

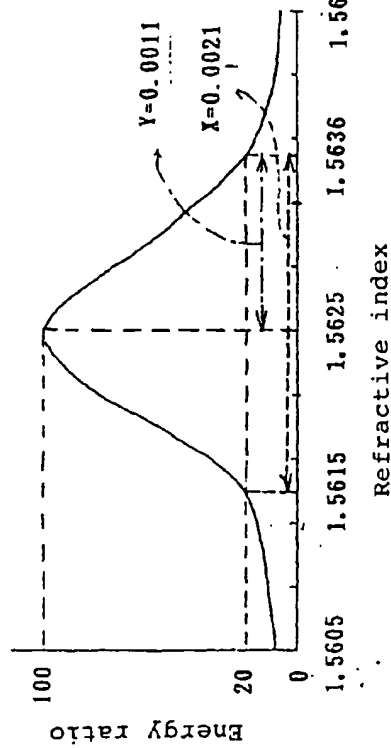


Fig. 13

